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ANALYSIS OF PARACHUTES SUSPECTED OF HAVING UNKNOWN SKIN IRRITANT CONTAMINATION (U)

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ABSTRACT

Parachutes contaminated with an unknown skin irritant were analysed and it was determined that significant levels of benzoic acid were present. Benzoic acid is a common, naturally occurring skin irritant, found in relatively high concentrations in berries, saps and gums. A gas chromatogram and electron-impact mass spectra are also provided.

RÉSUMÉ

Des parachutes contaminés avec un irritant de la peau inconnu furent analysés et on a déterminé qu'un niveau significatif d'acide benzoique était présent. L'acide benzoique est un irritant naturel et commun de la peau qui se trouve en concentration relativement élevée dans les baies, les sèves et les résines. Un chromatogramme d'analyse en phase gazeuse et un spectre de masse par impact d'électron sont aussi inclus.

1.0 INTRODUCTION

During training being held at Canadian Forces Base Petawawa during early June 1987, 150 soldiers were involved in a parachute jump exercise in which 9 soldiers landed outside of the designated jump zone. Three parachute packers in Edmonton later developed mild skin irritation on hands and arms while packing some or all of these 9 parachutes. The skin irritation was removed by washing.

Inspection of the approximate location of the landing spots for the stray jumpers revealed no indication of the spraying of defoliant. One member of the parachute packing team (1) suggested that the irritant could be from battery acid from the recovery team vehicle.

The Materials Chemistry Group at DREO was then asked (2) to perform some analyses in order to assess whether there were any significant levels of organophosphorus contaminants on 4 of the 'contaminated' parachutes. Two clean 'control' parachutes were also included in order to ensure that a false positive result would not occur.

2.0 EXPERIMENTAL

It was decided that for logistical reasons, only a few samples of the actual parachute material would be analyzed by destructive procedures such as soxhlet extraction. Two 'contaminated' parachutes and one control parachute were sampled and the remaining ones left intact.

When the parachutes were unpacked (after vapour sampling), it was noticed that there was a fair amount of pollen, sand, and other fine particulates on the material. It was apparent from the encrusted sand deposits, and the damp, musty odor that the parachutes had been exposed to water and/or rain. This very noticeable odor which resembled wet vegetation was not present in the comparatively new-looking control parachutes. From these observations it was apparent that the parachutes had indeed been exposed to wet vegetation and sand.

It was decided that the first assumption would be that the irritant is some organic compound (e.g. pesticide, defoliant, etc.) with a sufficient vapour pressure so that vapour sampling would be a feasible method. Since the parachutes were tightly bundled in polyethylene plastic bags (double bagged) it was decided that vapour within the bag should be analysed. This was performed in two ways, the simplest approach was by straight injection of the vapour into a gas chromatograph/mass spectrometer (GC/MS) in electron impact mode. The second option pursued was to cryogenically trap any desorbed organics in a liquid nitrogen cold trap. It was hoped that this preconcentration step would trap and therefore enhance the concentration of all organic compounds present in the vapour phase within the parachute bag. Sampling of the vapour from the two contaminated parachutes was performed for approximately 3 hours at approximately 100 mL/min.

The condensed sample was then sealed in a glass tube with a septum fitting and allowed to warm up to room temperature. Using gas-tight syringes, 25 to 50 µL injections were made into a GC/MS (Hewlett-Packard 5970B) equipped with a thick-film high resolution capillary column (30 m × 0.32 mm I.D. fused silica with 2 micron thick SPB-5 coating) and cryogenically cooled oven capability. All vapour analyses (i.e. for both the straight headspace within the parachute package and the cryogenically trapped sample) employed the following GC/MS operating conditions:

- electron multiplier voltage 1800V;
- quadrupole scan 45 to 300 m/e at ~1 sec/scan;
- detector temperature 270°C;
- transfer line temperature 250°C;
- oven program -30°C for 1 minute, 20°C/min ramp to 250°C, hold at 250°C for 3 minutes;
- all injections were performed splitless.

The second phase of the investigation addressed the possibility that the parachutes were contaminated with high levels of some involatile organic or inorganic compound such as a fertilizer or high molecular weight biological compound. In order to prepare a sample suitable for analysis it was decided that an aqueous and an alcoholic soxhlet extraction would be performed.

The aqueous soxhlet extraction was executed using a 10 inch by 10 inch sample of canopy material from one of the parachutes marked 'contaminated'. Approximately 125 mL of water was refluxed through the sample over 3 hours. The cloudy green extract was then concentrated to dryness using a roto-evaporator and then the water soluble component of the extract was taken up in deuterated water so that analysis using a nuclear magnetic resonance (NMR) spectrometer could be performed. Both proton and phosphorus 31 (to hopefully identify the presence of any phosphorus based fertilizer residue) NMR spectra were generated using a Varian XL-200 NMR spectrometer.

A similar procedure was performed using ethanol and another 10 in. by 10 in. sample of contaminated parachute canopy that was cut out at random. When the dark green extract was slowly evaporated down to dryness approximately 4-5 mg of clear, colorless leaflet and needle crystals were obtained. Due to the insufficient amount, a melting point determination was not attempted. The crystals were transferred to a NMR sample tube and dissolved with deuterated methanol.

A sample of the alcohol extract was also analysed by thin layer chromatography (TLC) using silica gel plates and ethanol/methanol developing solvent. This analysis was inconclusive because of the smearing effect of the parachute dye. Only one large spot was observed, even using ultra-violet light.

As for the aqueous extract, proton and phosphorus NMR spectra were also obtained using the XL-200. In addition, a 25 µL injection of the sample as it existed in the NMR tube (i.e. in deuterated methanol) was analysed by high resolution gas chromatography mass spectrometry. The operating conditions employed for the GC/MS analysis were identical to those described previously for the vapour analyses except for the following differences:

- oven program 50°C for 1 minute, 20°C/min ramp to 250°C, hold for 3 minutes;
- all injections were performed splitless, solvent delay for 2 minutes before starting data acquisition;
- injections were 1 µL.

A summary of the analyses performed is outlined in Annex 1.

3.0 RESULTS AND DISCUSSION

3.1 HEADSPACE ANALYSIS

All GC/MS analyses of the headspace within the contaminated parachute package were negative for the presence of any volatile organic compounds with irritating properties and in significant concentrations. It was assumed from the outset that if the contaminant is in a concentration

that is less than the high sensitivity that the GC/MS is capable of (picograms), the contamination would not be a problem.

Analysis of the cryogenically trapped headspace vapours indicated only the presence of water and an assortment of innocuous phthalates which are common to polymeric materials (probably from the polyethylene bag, more than anywhere else). The condensate was clear and colorless and had a pH of 5-6. Hence it was tentatively concluded that the skin-irritating contaminant, if it was present, was likely to have low volatility at room temperature.

3.2 SOXHLET EXTRACTIONS

Two of the contaminated parachutes were carefully unpackaged and laid out for examination. Small (10 in. by 10 in.) sections of the canopy were cut out and placed in individual sample bags. The parachutes were carefully examined for any signs of visible or odorous contamination and pieces of the canopy and harness which contained any discoloration or obvious residues were obtained. Remarkably, the drab green dye was very easily removed by water extraction. The resulting cloudy green extract was found to have a pH of 3.7. This level of acidity may or may not be significant since rain water has been known to have pH's as low as 4.0. The ethanol extraction removed even more dye and was opaque green in color.

It was decided that for both extractions, the solvent would be evaporated out and replaced with a deuterated solvent so that NMR could be performed. Subsequent to this, GC/MS analyses would also be performed on the extracts taken up in deuterated solvent.

3.3 NMR ANALYSIS

Both extracts were concentrated and analysed using multi-nuclear NMR. Proton, carbon-13, and phosphorus-31 NMR spectra were obtained and, in all instances, found to have no indication of any contaminants. However, it should be noted that the comparatively low sensitivity of this instrument could be the sole reason for the negative result. The objective of the NMR analysis was more of an attempt to identify any high levels of contamination which could have existed. In particular, it was hoped that the presence of an inorganic compound such as a phosphorus-containing fertilizer, would be made obvious by this analyses.

3.4 GC/MS ANALYSES

Analysis of the aqueous extract (taken up in D_2O) by high resolution gas-liquid chromatography/electron-impact mass spectrometry revealed no obvious contaminants. The only compounds detected were due to the green dye. This result was not surprising since most organic irritants are not highly soluble in water.

The crystalline residue obtained from the ethanol extraction was also analysed by GC/MS and the presence of a significant level of benzoic acid was clearly determined (see Figures 1,2 and 3). Since the solvent was replaced with deuterated methanol, the mass spectrum shows a 50:50 ratio of ion 122 and 123 due to exchange between the hydroxyl proton on the benzoic acid molecule and the deuterium from the deuterated methanol solvent. The occurrence of this phenomenon provided additional confirmation of the molecule's identity. If the solvent employed were non-deuterated, the intensity of ion 122 would be equal to the sum of 122 and 123 in Figure 2 so that the resulting spectrum would then have been nearly identical to that of benzoic acid from the NBS library (Figure 3).

Benzoic acid is highly soluble in alcohols and has low solubility in water; this explains the absence of this compound in the aqueous extract. Benzoic acid's boiling point of 122°C also explains the negative results obtained in the headspace vapour analyses.

Benzoic acid is very common in nature, particularly in berries, saps, and gums which may contain levels up to 20% (3). It is also reported in the Merck Index, that benzoic acid is a mild irritant to skin, eyes and mucous membranes (see Annex 2). However this compound, in addition to being common in nature, is also used as an anti-fungal agent and is often used in manufacturing dyes. Therefore the origination of this contaminant in the parachutes remains speculative.

3.5 CONTROL PARACHUTE ANALYSIS

A 10 in. by 10 in. sample of the canopy from an uncontaminated (control) parachute was obtained and an ethanol soxhlet extraction performed. The sample was treated identically to that of the contaminated parachute samples for which benzoic acid was determined.

No crystalline product was found in the extract, and no indications of any organic compounds of significance were detected by

FIGURE 1

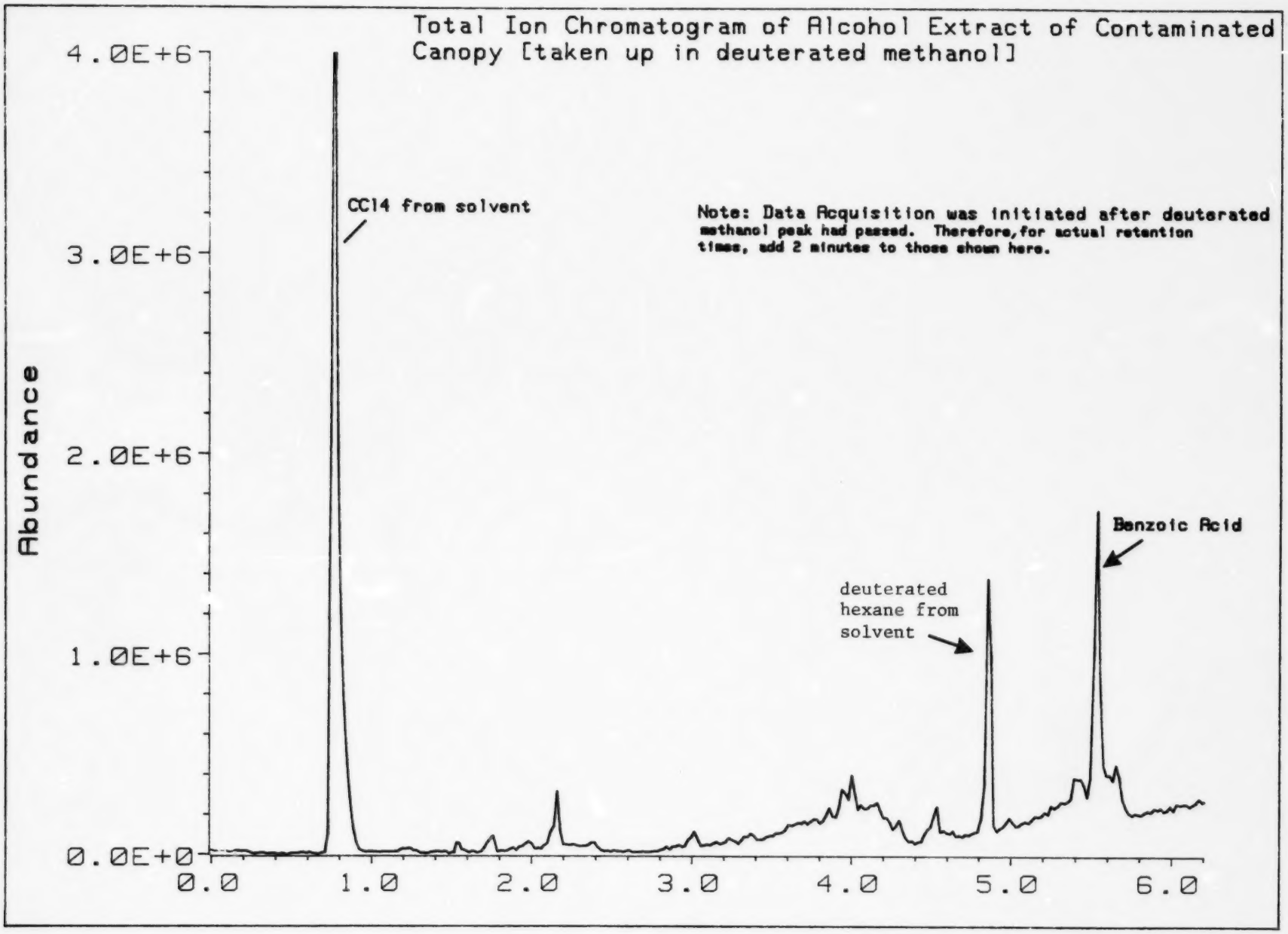

Total Ion Chromatogram of Alcohol Extract of Contaminated Canopy [taken up in deuterated methanol]
Abundance
4.0E+6
3.0E+6
2.0E+6
1.0E+6
0.0E+0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
CCl4 from solvent
Note: Data Acquisition was initiated after deuterated methanol peak had passed. Therefore, for actual retention times, add 2 minutes to those shown here.
deuterated hexane from solvent
Benzoic Acid

FIGURE 2

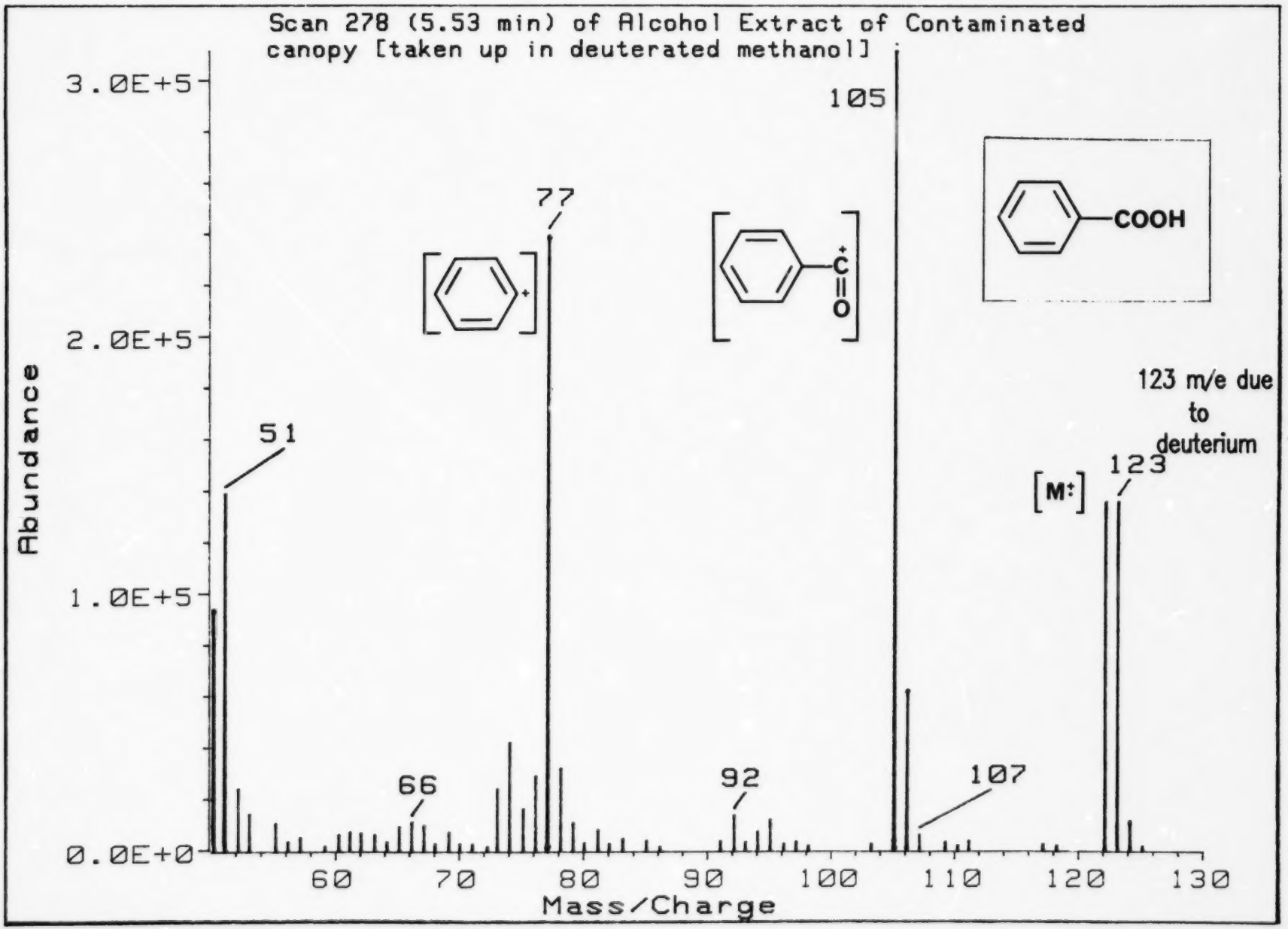
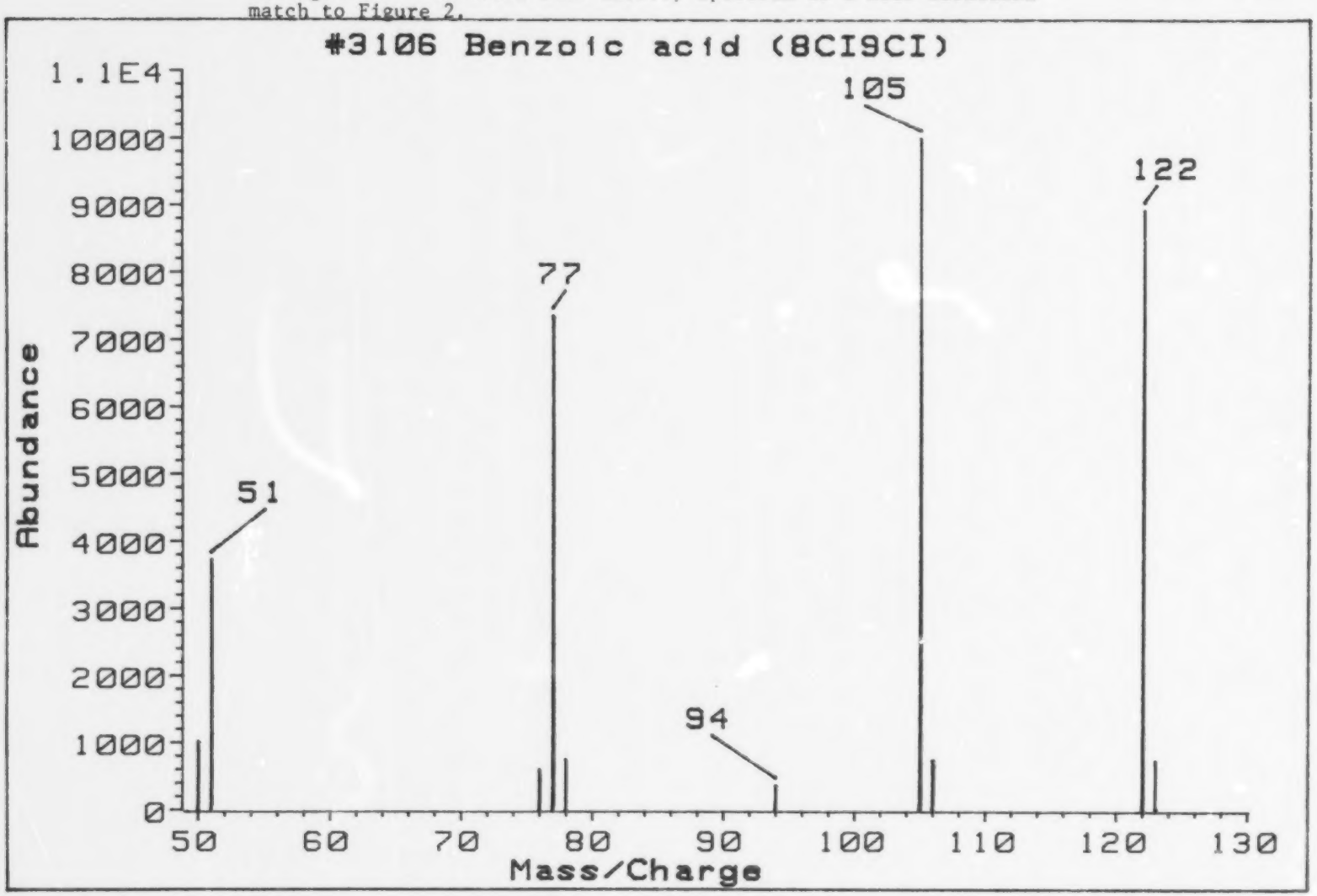

Scan 278 (5.53 min) of Alcohol Extract of Contaminated canopy [taken up in deuterated methanol]
Abundance
3.0E+5
2.0E+5
1.0E+5
0.0E+0
105
77
51
66
92
107
123
[M:]
123 m/e due to deuterium
COOH
60
70
80
90
100
110
120
130
Mass/Charge

FIGURE 3

NBS Library mass spectrum for benzoic acid. Note that since there is no deuterium, the relative intensity of ion 122 in this spectrum is much greater. Otherwise this library spectrum is a near identical match to Figure 2.



GC/MS. It was also noted that the control parachutes were comparatively odorless (no musty odor).

4.0 CONCLUSIONS

The general conclusion of this investigation is that there is significant evidence that the skin-irritating contaminant present on the parachutes belonging to the soldiers that landed outside of the designated jump zone, is benzoic acid. The estimated 4-5 mg per square foot of material is concluded to be a significant level of contamination. Therefore, it is highly probable that the benzoic acid contamination originates from the wild vegetation that the stray paratroopers must have landed near and dragged their canopies through.

It is also concluded that there were no obvious pesticides, herbicides or volatile irritants on the contaminated parachutes.

The presence of a large amount of pollen and other particulates in addition to the strong musty odor of vegetation provides evidence that there still exists the possibility that the skin irritant could have been due to an allergic reaction or a response to natural irritants (very high molecular weight) found in various forms of wild grasses and weeds.

Finally, it is also concluded that although it appears that the contaminant is indeed benzoic acid, it is highly possible that the actual contaminant may be localized to some very small section of one of the parachutes that could have been overlooked. The logistics of obtaining enough samples from the enormous surface area which a parachute has, so that a representative analysis could be performed, would be extremely labor intensive.

5.0 RECOMMENDATIONS

It is recommended that, given that the skin irritation was very mild, and easily removed by washing, the contaminated parachutes be laundered with cold water and mild soap, and then repaired and re-issued for service.

It is also recommended that proper sampling techniques be employed on-site if this situation re-occurs and contaminant identification is required. The enormous size of the suspected contaminated material is far too difficult to analyze in a meaningful manner unless visible residues are present which can be cut out and concentrated on.

6.0 REFERENCES

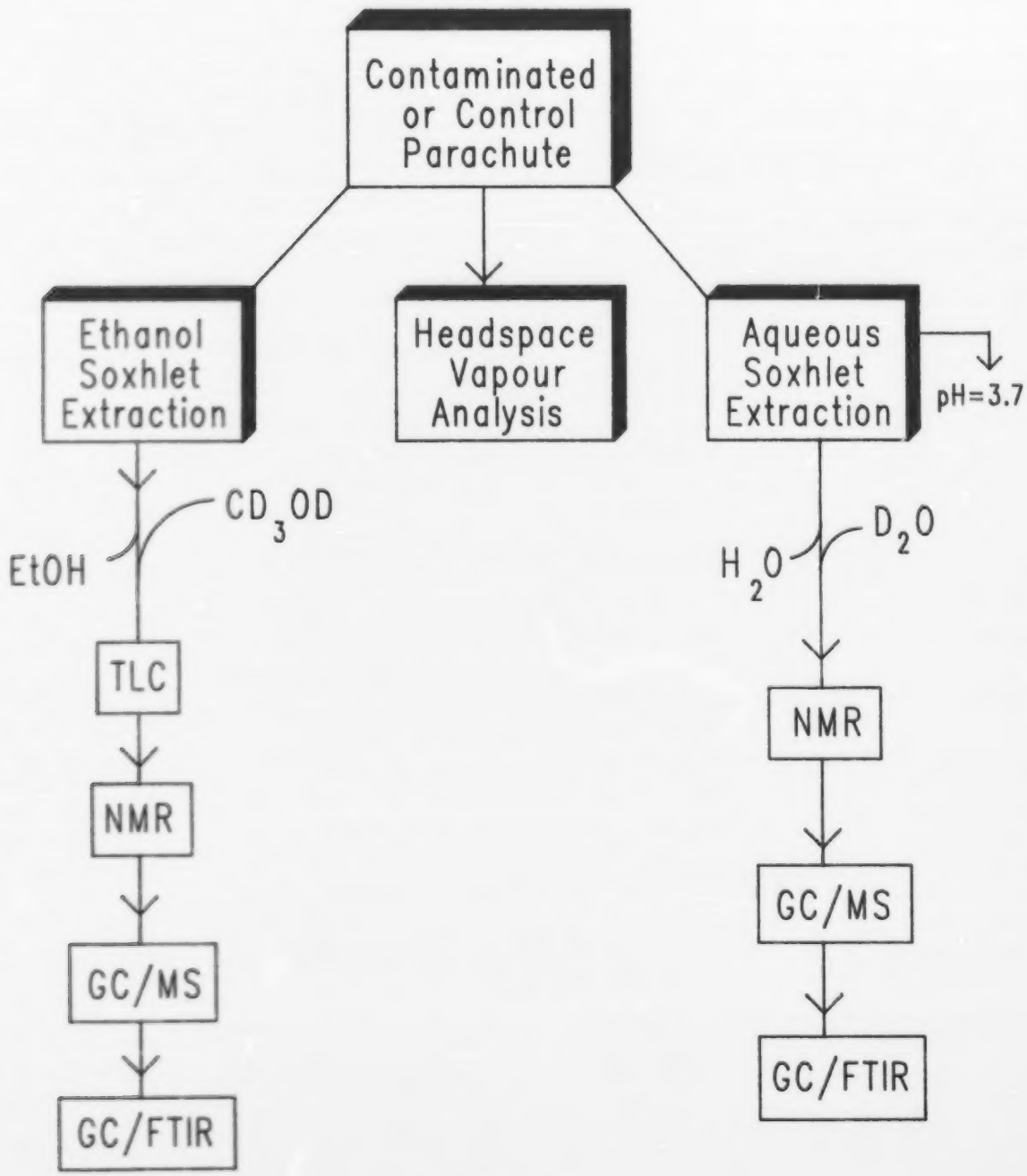
1. CWO Steward personal communication with E. Nilsen, QETE (Q3-5-2).

2. Telecon E. Nilsen/J. Pagotto, 4 August 1987.

3. Merck Index, 8th ed.; (Annex 2).

ANNEX 1

Flowsheet for Analysis of Contaminated Parachutes



ANNEX 2

Benzoic Acid. Benzenecarboxylic acid; phenylformic acid; dracylic acid. $C_7H_6O_2$; mol wt 122.12. C 68.84%, H 4.95%, O 26.20%. Occurs in nature in free and combined forms. Gum benzoin may contain as much as 20%. Most berries contain appreciable amounts (around 0.05%). Excreted mainly as hippuric acid by almost all vertebrates, except fowl. The manuf of benzoic acid is discussed in *Kirk-Othmer's Encyclopedia of Chemical Technology*, vol. 3 (2nd ed, Interscience, 1964), p 423–426. Processes described include the air oxidation of toluene, the hydrolysis of benzotrichloride, and the decarboxylation of phthalic anhydride. Laboratory prepn from benzyl chloride: A. I. Vogel, *Practical Organic Chemistry*, (3rd ed, Longmans, London, 1959), p 755; from benzaldehyde: Gattermann-Wieland, *Praxis des organischen Chemikers*, (40th ed de Gruyter, Berlin, 1961), p 193. Prepn of ultra-pure benzoic acid for use as titrimetric and calorimetric standard: Schwab, Wicher, *J. Research Natl. Bur. Standards* **25**, 747 (1940).

Monoclinic tablets, plates, leaflets. Perfect 001 cleavage. d 1.321 (also reported as 1.266). mp 122.4°. Begins to sublime at around 100°. bp_{760} 249.2°; bp_{400} 227°; bp_{200} 205.8°; bp_{100} 186.2°; bp_{50} 172.8°; bp_{40} 162.6°; bp_{20} 146.7°; bp_{10} 132.1°. Volatile with steam. Flash pt 121–131°. K at 25° = 6.40×10^{-5}; pH of satd soln at 25° = 2.8. Solubility in water: At 0° = 1.7 g/l; at 10° = 2.1 g/l; at 20° = 2.9 g/l; at 25° = 3.4 g/l; at 30° = 4.2 g/l; at 40° = 6.0 g/l; at 50° = 9.5 g/l; at 60° = 12.0 g/l; at 70° = 17.7 g/l; at 80° = 27.5 g/l; at 90° = 45.5 g/l; at 95° = 68.0 g/l. Mixtures of excess benzoic acid and water form two liquid phases beginning at 89.7°. The two liquid phases unite at the critical soln temp of 117.2°. Composition of critical mixture: 32.34% benzoic acid, 67.66% water: *see* Ward, Cooper, *J. Phys. Chem.* **34**, 1484 (1930). One gram dissolves in 2.3 ml cold, 1.5 ml boiling alcohol, in 4.5 ml chloroform, 3 ml ether, 3 ml acetone, 30 ml carbon tetrachloride, 10 ml benzene, 30 ml carbon disulfide, 23 ml oil of turpentine; also sol in volatile and fixed oils, slightly in petr ether. The soly in water is increased by alkaline substances, such as borax or trisodium phosphate, *see also* Sodium Benzoate. LD orally in dogs: 2 g/kg (tested as sodium benzoate).

USE: Preserving foods, fats, fruit juices, alkaloidal solns, etc; manuf benzoates and benzoyl compds, dyes; as a mordant in calico printing; for curing tobacco. As standard in volumetric and calorimetric analysis.

MED USE: Antifungal agent. *Dose:* 6% concn with 3% salicylic acid in ointment. *Human Toxicity:* A mild irritant to skin, eyes, mucous membranes.

VET USE: Together with salicylic acid in ointments for the treatment of ringworm in dogs and other species.

Excerpt from Merck Index, Eighth Edition. Note the high concentrations of benzoic acid (20%) found in nature, its commercial uses, and the reported skin irritancy.

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